

B<sup>2</sup>  
concl'd  
substrate MGP with minor decrease in activity. The  
elemental analysis after oxidative runs did not detect  
any nitrogen, thus establishing the lack of leaching of  
the entrapped nitroxyl radicals in the reaction solution.

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IN THE CLAIMS ✓

Cancel claim 13 without prejudice or disclaimer  
and enter the following new claims:

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22. (New) A process for the preparation of a  
reactive sol-gel catalytic porous material comprising  
chemically doping said material with stable organic  
nitroxyl radicals, by carrying out the steps of:

copolymerizing a solution including:

a) 3-amino-propyl-trimethoxysilane as a monomer  
precursor;

b) a dopant consisting of 4-oxy-TEMPO as a  
stable nitroxyl radical or a precursor thereof;

B<sup>3</sup>  
c) a solvent including H<sub>2</sub>O and a co-solvent  
selected from the aliphatic alcohols; an acid or base to  
catalyze the processes of sol-gel hydrolysis and  
copolymerization; and one or more additives selected from  
those known to be useful in the preparation of porous  
materials to form a gel containing said dopant trapped  
therein;

d) tethering said radical to said monomer precursor through reductive amination, said solution including H<sub>2</sub>O as a solvent and a co-solvent from the aliphatic alcohols; an acid or base to catalyze the processes of sol-gel hydrolysis and copolymerization; and one or more additives selected from those known to be useful in the preparation of porous materials to form a gel containing said dopant chemically trapped therein;

e) evaporating said solvent;

f) drying said gel; and

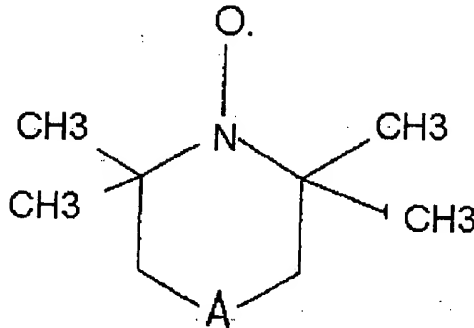
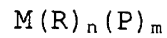
g) coating said gel on a mesoporous inorganic support.

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cont'd

23. (New) A process for a liquid-phase oxidative conversion of a substrate of a primary or secondary alcohol into a carbonyl or carboxyl derivative thereof, comprising said conversion being carried out with said substrate in catalytic presence of a reactive sol-gel catalytic porous material either chemically or physically doped with stable organic nitroxyl radicals, said material being coated on a mesoporous inorganic support and containing a copolymer of

a) at least one monomer precursor selected from the group consisting of metal and semi-metal alkoxides,

metal esters and semi-metal esters, of the general  
formula



wherein M is a metal or a semimetal, R is an hydrolyzable  
substituent, P is a non-hydrolyzable group, n is an  
integer of 1 to 6, and m is an integer of 0 to 6, and

b) a dopant consisting of a stable di-tertiary-  
alkyl nitroxyl radical or a precursor thereof of formula,  
wherein A represents a chain of two or three carbon  
atoms, one or two of said carbon atoms being eventually  
substituted by one oxygen or nitrogen atom, and one or  
more additives selected from those known to be useful in  
the preparation of porous materials to form a gel  
containing said dopant trapped therein.

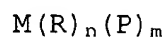
✓  
Please amend claim 1 as follows:

1. (Twice Amended) A process for the  
preparation of reactive sol-gel catalytic porous  
materials either chemically or physically doped with

stable organic nitroxyl radicals, comprising the steps  
of:

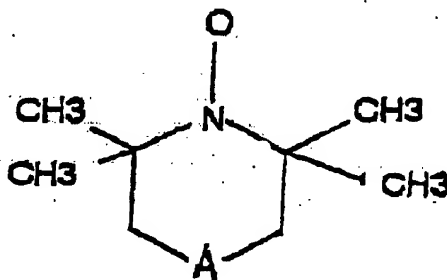
a) copolymerizing a solution including:

at least one monomer precursor selected from  
the group consisting of metal and semi-metal alkoxides,  
metal esters and semi-metal esters, of the general  
formula



wherein M is a metal or a semimetal, R is an hydrolysable  
substituent, P is a non-polymerizable group or a non-  
hydrolyzable substituent, n is an integer of 1 to 6, and  
m is an integer of 0 to 6,

a dopant consisting of a stable di-tertiary-  
alkyl nitroxyl radical or a precursor thereof of formula



wherein A represents a chain of two or three  
carbon atoms, one or two of said carbon atoms being  
eventually substituted by one oxygen or nitrogen atom,

a solvent including H<sub>2</sub>O and a co-solvent  
selected from the aliphatic alcohols;

an acid or base to catalyse the processes of  
sol-gel hydrolysis and copolymerization; and

one or more additives selected from those known  
to be useful in the preparation of porous materials  
to form a gel containing said dopant trapped  
therein;

b) evaporating said solvent;

c) drying said gel;

d) coating said gel on a mesoporous inorganic  
support; and

e) drying said mesoporous material coated with  
said sol-gel.

✓  
Please amend claim 3 as follows:

3. (Third Amendment) The process according to  
claim 22, wherein said non-hydrolyzable substituent is H,  
an alkyl, aryl or fluoroalkyl group or an aminoalkyl  
group.

[Please amend claim 4 as follows:]

4. (Third Amendment) The process according to  
claim 22, wherein said step c) of drying the gel is a  
liophilisation carried out at a pressure lower than 70 mm  
Hg, to obtain a mesoporous aerogel powder.

[Please amend claim 5 as follows:]

B<sup>5</sup>  
could

5. (Third Amendment) The process according to claim 22, wherein said step c) of drying the gel is a mild heat treatment carried out at an atmospheric pressure and a temperature no greater than 100°C.

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✓  
Please amend claim 6 as follows:

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6. (Amended) The process according to claim 22, wherein said nitroxyl radical is added to said solution along with said monomer precursor in a one-step procedure.

B<sup>6</sup>

[Please amend claim 7 as follows:]

7. (Amended) The process according to claim 22, wherein in a two-step procedure, first said monomer precursor is hydrolyzed in part with water in the presence of an acid and then said nitroxyl radical is added to this solution, to obtain a porous sol-gel polymeric oxide with a fractal macromolecular structure.

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✓  
Please amend claim 9 as follows:

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9. (Amended) The process according to claim 22, wherein said reductive amination is carried out by stirring a solution of said 4-oxo-TEMPO in methanol with

B7  
cond said 3-aminopropyl-trimethoxysilane, and reducing the  
thus formed imine with  $\text{NaBH}_3\text{CN}$ .

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✓  
Please amend claim 11 as follows:

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B8  
11. (Twice Amended) The process according to  
claim 22, wherein said catalytic porous materials are in  
the shape of powders, films, monoliths, or fibers.

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✓  
Please amend claim 14 as follows:

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B9  
14. (Amended) A process according to claim 23,  
wherein said liquid phase is an organic solvent, a  
biphasic organic solvent-water system, or water and said  
primary oxidant is  $\text{NaOCl}$ ,  $\text{NaOBr}$ ,  $\text{HNO}_3$ ,  $\text{CuCl}/\text{O}_2$ ,  $\text{K}_3\text{Fe}(\text{CN})_6$ ,  
or  $\text{NO}_2$ .

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✓  
Please amend claim 15 as follows:

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B10  
15. (Third Amendment) A process according to  
claim 23, wherein said alcohol substrate is an alkyl  
alcohol, an aryl alcohol, a steroid alcohol, an allylic  
alcohol, a terpenoid alcohol or retinol and it is  
oxidized in a bi-phasic reaction system  $\text{CH}_2\text{Cl}_2\text{-H}_2\text{O}$ , said  
primary oxidant is aqueous alkaline  $\text{NaOCl}$  and wherein  
said nitroxyl radical is 4-oxy-TEMPO and said monomer  
precursor is 3-aminopropyl-trimethoxysilane to obtain a  
catalytic material containing chemically linked radicals.

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✓  
Please amend claim 16 as follows:

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16. (Twice Amended) A process according to claim 23, wherein said alcohol substrate is a monomer or an oligomeric carbohydrate protected at the anomeric center, said solvent is water, said oxidant is alkaline NaOCl or NaOCl in the presence of a catalytic amount of NaBr, and wherein said nitroxyl radical is 4-oxy-TEMPO and said monomer precursor is 3-amino-propyl-trimethoxysilane to obtain a catalytic material containing chemically linked radicals.

✓  
Please amend claim 18 as follows:

B<sup>12</sup>  
18. (Twice Amended) The catalytic material doped with a chemically linked nitroxyl radical obtained with a process as claimed in claim 22.

✓  
Please amend claim 21 as follows:

B<sup>13</sup>  
21. (Amended) A process according to claim 23, wherein said alcohol substrate is an alkyl alcohol, an aryl alcohol, a steroid alcohol, an allylic alcohol, a terpenoid alcohol or retinol and it is oxidated in a bi-phasic reaction system  $\text{CH}_2\text{Cl}_2\text{-H}_2\text{O}$ , wherein said primary oxidant is aqueous alkaline NaOCl, and wherein said nitroxyl radical is 4-oxy-TEMPO and said monomer



precursor is 3-aminopropyl-trimethoxysilane to obtain a catalytic material containing chemically linked radicals, wherein said radical is tethered to said monomer precursor through reductive amination by stirring for three hours a solution of 4-oxo-TEMPO in methanol with a slight excess of 3-aminopropyl-trimethoxysilane, and reducing the thus formed imine with  $\text{NaBH}_3\text{CN}$ .

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